METAL IONS/OXIDES TETHERED GRAPHITIC CARBON NITRIDE: SYNTHESIS, CHARACTERIZATION AND CATALYTIC APPLICATIONS IN AQUEOUS MEDIUM

A SYNOPSIS

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1. INTRODUCTION

It is known that one of the science and technology of inducing the rates of chemical reactions is catalysis. In general, catalysts are materials which are changing the track of a chemical reaction with no expansion itself. Consequently, a small quantity of catalytic material can transform a huge quantity of substrates (reactants) into their corresponding products and mostly this type of processes happens favorably under mild conditions than would be needed by the pathway of stoichiometric reaction. In case of reactions where more than one product is probable, the catalytic process may culminate with distribution of outcomes towards selective ones reflecting selectivity of the reaction [1]. Reactions of catalysis are not only at the nucleus of production of most materials and chemicals, but also play a vital role in older and new energy applications, in controlling pollution, in production of food, and in medical applications [2].

As for as the industrial community is concerned, several attentions have been dedicated in order to reduce energy consumption as well as energy emission. Further, for any method of industrial utility, attention needs to be paid on usage of non-toxic / less toxic solvents, lower reaction temperature, easy recovery of the products, minimization of side products and wastage [3]. Since greater than 90% of the chemical reactions involve the employment of catalysts, it is obvious that the essential task for catalytic exploration is to develop more superior catalysts [4].

On comparing the heterogeneous catalysts, homogeneous catalysts commonly possess better activity or / and selectivity. However, the primary concern of catalyst separation from the reactants and products rigorously limits their actual application when it comes to the industrial applications. On the other hand, heterogeneous catalysts are generally stable and those can readily be isolated from a reaction mixture [5]. Hence, it is largely believed that an ultimate solution to connect the gap between homogeneous and heterogeneous catalysis is the heterogenization of homogeneous catalyst (i.e., anchoring a catalyst on an insoluble support in order to enjoy the benefits of both homogeneous and heterogeneous catalysts [6]). However, research in the past decades implies that this is quite challenging to some extent [7].

Graphitic carbon nitride (GCN), a readily available, stable and eco-compatible material, attracted much attention by the researchers around the globe. Tunable

optoelectronic properties is one of its favorable attributes. Several routes have been utilized to synthesize graphitic carbon nitride, however, the method of pyrolysis has been used to construct bulk graphitic carbon nitride from any nitrogen rich precursor, viz., urea [8], thiourea [9], melamine [10], and cyanamide [11].

The defined building of graphitic carbon nitride comprises of two core units, such as, s-triazine (C_3N_3) and tri-s-triazine (C_6N_7) rings (Figure. 1.1) [12,13]. Under ambient conditions, tri-s-triazine has been recognized to be more stable [14]. Theoretical investigation further supports that tri-s-triazine is thermodynamically most stable as evidenced from density functional theory (DFT) calculations.

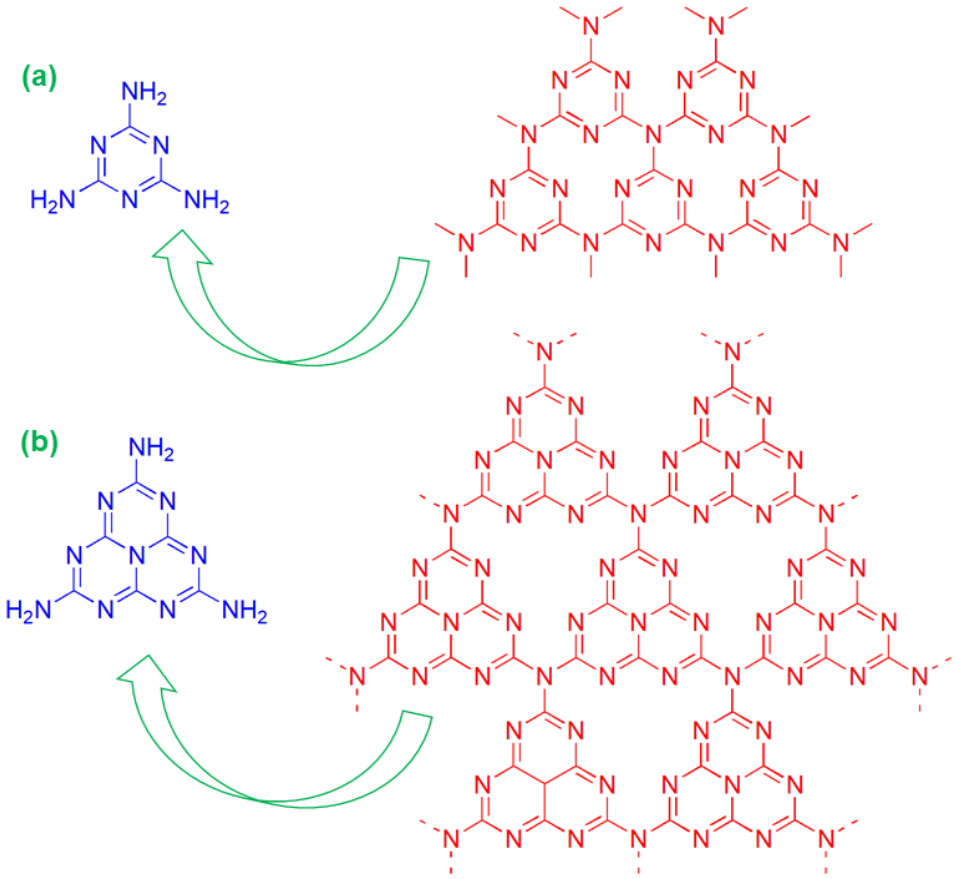

Figure 1.1 Graphitic carbon nitride (GCN): (a) s-triazine and (b) tri-s-triazine-based structures.

Due to the appealing properties of GCN including biodegradability, sustainability, appropriate tunable narrow band gap and electron-rich properties, it has been applied in a range of fields including photocatalysis, sensing, energy storage, solar cells and organic synthesis.

2. LITERATURE REVIEW

Organic synthesis: Organic synthesis has traditionally been an influential tool for the synthesis of various drug molecules, agrochemicals, natural products, polymers and a diverse other materials. Nevertheless, designing an organic reaction is as similar as designing a catalyst. Catalysts generally play a vital role in synthetic organic chemistry through bond breaking and bond making processes. De et al. [15], Di Liberto et al. [16], Choudhary et al. [17], Xu et al. [18]. As known, there are two major types of catalysis in use: one is homogeneous catalysis and heterogeneous catalysis is the other and, both have their own advantages. For instance, a solution possessing molecularly-defined organometallic complexes (homogeneous) and metals possessing solid catalysts are the two types. Cambie et al. [19], Kerackian et al. [20], Degennaro et al. [21], Borgamans et al. [22]. Despite the admirable selectivity and activity, the former category have various hitches which include expensive and lengthy ligand design, separation of complex ensuring recovery of metal, higher level of sensitivity of the target molecule with respect to moisture and air, and tasks with respect to stability of catalyst. Li et al. [23] Consequently, scientists around the globe have tried immobilizing organometallic complexes on solid supports in order to decipher a few or all those issues. Mosrati et al. [24], Harmel et al [25]. In the recent past, exceptional performance for diverse reactions has been demonstrated through surface organometallic catalysis. Particularly, these catalytic systems have been proposed as a uniting concept bridging metals and organometallic catalysis. Mitchell et al. [26], Singh et al [27].

Buker et al [28] developed copper integrated GCN catalyst through a two-step method and the catalyst exerted potent activity towards the oxidation of cyclohexene using molecular oxygen as an oxidant. The oxidation state of Cu was Cu(I). The catalytic activity is similar to that of the homogeneous Cu(I), however, the heterogeneous character of the catalyst prominently simplified its recovery.

Vile and co-workers [29] developed copper tethered mesoporous GCN and this material was utilized as an effective catalyst for the one-pot three component reaction between an alkyne, an azide and an halide to afford 1,2,3-triazoles, known as click reaction, under base free condition. The catalyst was synthesized through tricyanomethanide polymerization in order to harvest a joint electronic structure

wherein the mpGCN acts as a ligand of multidentate nature. On compared with homogeneous catalytic activity, this copper catalyst ends up with enhanced catalytic activity.

Chen et al [30] developed another exciting application utilizing a top-down pyrolysis method on natural wood in order to synthesize iron, cobalt, nickel and copper integrated porous carbonaceous support. Of all those, iron integrated one demonstrated as an efficient catalyst for the construction of substituted quinolones from acetophenones, anilines and DMSO through one-pot three component cyclization reaction. As an extension, this method was utilized to construct cavosonstat (cyctic fibrosis transmembrane conductance regulator – an orally bioavailable one).

Platinum integrated GCN was synthesized by He et al [31] and employed as an efficient catalyst for the hydrogenation of nitro arenes to anilines in a chemoselective manner under visible light condition. Ma and co-workers [32] explored an unusual reaction with the utilization of nickel tethered GCN. After developing the nickel based catalyst, they utilized the same for the synthesis of imines from benzyl alcohol and a wide variety of amines, an unusual method when compared with the general method of synthesis of imines, usually synthesized by the condensation of carbonyl compounds and amines.

Photocatalysis: The capability of GCN in producing solar energy because of its suitability of band gap has made feasible its utility as a photocatalyst. Zhao et al. [33], Shen et al. [34]. Bulk GCN has limitations of only blue light absorption (450 nm), however, due to a low surface area, comparatively wide band gap (approx. 2.7 eV), and fast charge recombination rate, various alterations have been made in order to advance and optimize the absorption of light. These comprise doping, dye-sensitization and copolymerization. GCN photo catalysts have classically been applied in a couple of main areas viz., water splitting to form O_2 and H_2 and the pollutants degradation.

Huang et al [35] used WO_3 immobilized GCN and Haung et al [36] used MoO_3 integrated GCN as catalysts for the photodegradation of methylene blue, a salt possessing phenothiazine structural motif primarily utilized as a dye and as a medication under UV light.

Paul and co-workers [37] studied the effect of pH, calcination temperature, and loading of catalyst on the efficiency of photodegradation of GCN towards a dye solution, methylene blue and delightfully, it was observed that the calcination temperature for the GCN synthesis along with the aforementioned factors such as catalyst loading and pH significantly influenced the photodegradation.

La_2O_3 integrated GCN was synthesized by Xie et al [38] by adopting a facile single-step hydrothermal methodology and demonstrated as an efficient photocatalyst for the degradation of different organic pollutants such as methylene blue, methyl orange and rhodamine B under UV light. This composite proved to be better photocatalyst when compared to the GCN and the incorporation of La_2O_3 considerably enhanced the surface area of GCN.

Fabrication of ternary composites, reduced graphene oxide / titania / graphitic carbon nitride (rGO/TiO_2/ GCN) has been made from the mixture of TiO_2 nanoparticles, reduced graphene oxide and GCN by Lin et al [39]. Among the ternary nanocomposites with varying amount of GCN, the one rGO/TiO_2/CN-$_{0.75}$ composite was found to be the best one towards the photo degradation of methylene blue under UV light.

Concisely, development of economically beneficial, environmentally benign, and recyclable catalysts for a diverse range of applications, in general, is still vital and, various research communities around the globe are prosecuting their research in line with the aforementioned statement. Metal ions / metal oxides tethered on solid support belongs to one of the categories of catalysts which fall under the above category. Particularly, developing the aforementioned type catalysts for carbon-carbon bond forming reactions in one side and degradation of organic pollutants on the other side are a couple of significant needs of the globe. Having these two important needs in mind, the present piece of research is designed and executed.

3. OBJECTIVES

The objectives of the present investigation are

1) To synthesize cerium immobilized graphitic carbon nitride, characterize and demonstrate as a proficient catalyst for the synthesis of homo/hetero-

arylidenemalononitriles/malonic acid/cyanoester through construction of carbon-carbon double bond.

2) To synthesize iron integrated graphitic carbon nitride, characterize and apply as an efficient catalyst for the synthesis of bis(hetero/homoarylidene) cycloalkanones through construction of carbon-carbon double bond.

3) To synthesize palladium decorated graphitic carbon nitride, characterize and demonstrate as a pragmatic catalyst for the synthesis of bis(hetero/ homoarylidene/alkylidene)-1-alkylpiperidin-4-ones through construction of carbon-carbon double bond.

4) To synthesize alumina surface modified with graphitic carbon nitride, characterize and apply as a competent photocatalyst for the degradation of organic dye, methylene blue under direct sunlight.

5) To synthesize ceria surface modified with graphitic carbon nitride, characterize and demonstrate as an adept photocatalyst for the degradation of organic dye, methylene blue under direct sunlight.

4. RESEARCH PROBLEM

Generally, methodology development is a key in organic synthesis. Development of any methods with greener approach is one of the essential requirement to be considered by the researchers while prosecuting their research as it is directly related to environment. Developing recoverable catalysts and utilizing water as a medium for any type of reactions fall towards greener approach. In an effort to develop heterogeneous catalysts for carbon-carbon bond forming reactions, cerium immobilized graphitic carbon nitride, iron integrated graphitic carbon nitride, and palladium decorated graphitic carbon nitride were synthesized and utilized for the efficient construction of diverse ranges of homo/heteroarylidenemalononitriles/malonic acid/cyanoester, bis(hetero/ homoarylidene) cycloalkanones, and bis(hetero/ homoarylidene/ alkylidene)-1-alkylpiperidin-4-ones, respectively. In all the cases, the reactions were proceeded well in aqueous medium, an environmentally benign one at ambient temperature and the catalysts are recoverable atleast for five consecutive

cycles. Plausible mechanisms have been proposed. Further, alumina surface modified with graphitic carbon nitride, and ceria surface modified with graphitic carbon nitride were synthesized and employed as efficacious catalysts for the degradation of methylene blue, one of the largely utilized dyes in industries, under direct sun light. These catalysts are recoverable for atleast five consecutive cycles and the degradation process was proceeded in aqueous medium. The results are discussed in detail.

5. ORGANIZATION OF THE THESIS

Chapter 1:

This chapter describes a brief introduction about catalysis, heterogeneous catalysis, and carbon supports. It also discusses the significance of graphitic carbon nitride (GCN) and its geometrical, electronic structure, modifications to improve efficiency, and its applications towards organic synthesis and photodegradation.

Chapter 2:

It reviews the reported literature in connection with various metal / metal oxide tethered with graphitic carbon nitride utilized as a catalyst in the organic synthesis and photodegradation of organic dyes.

Chapter 3:

Chapter 3 describes the experimental part. Synthesis of metal ions (Cerium, Iron and Palladium) immobilized graphitic carbon nitride as an efficient catalyst to the synthesis of various bio pertinent molecules such as homo/heteroarylidene-malononitriles/malonic acid/cyanoester, bis(hetero/ homoarylidene)cycloalkanones, bis(hetero/homoarylidene/alkylidene)-1-alkyl- piperidin-4-ones and synthesis of metal oxide (alumina and ceria) surface modified with graphitic carbon nitride to utilize as a catalyst for photodegradation of methylene blue under direct sunlight.

Chapter 4:

This chapter presents the results and discussion on characterization of cerium immobilized graphitic carbon nitride by utilizing various spectroscopic and microscopic methods. Also, it describes the application of this heterogeneous catalyst for the construction of a diverse range of homo/heteroarylidenemalononitriles/malonic acid/cyanoester from their corresponding carbonyl precursors and respective active

methylene compounds in water, a green solvent at ambient temperature. The model reaction chosen is furnished in Figure. 1.2.

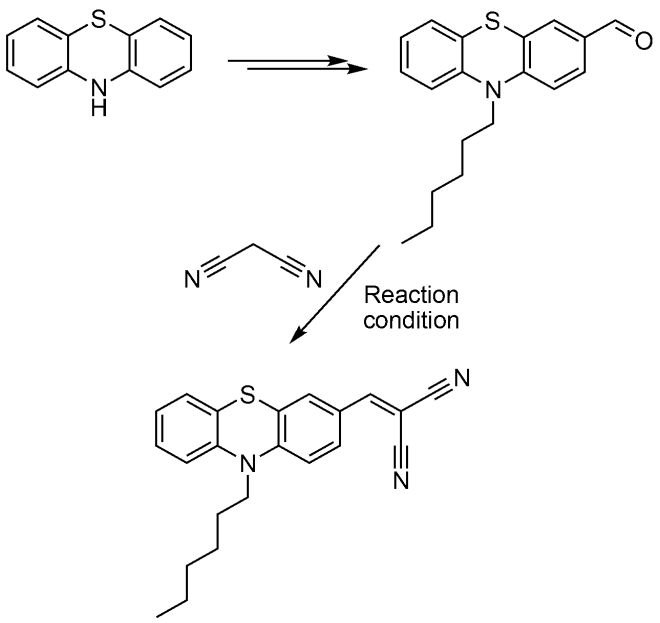

Figure 1.2 Model reaction for the construction of homo/heteroarylidenemalononitriles

Chapter 5:

It explains the results and discussion on characterization of iron integrated graphitic carbon nitride by adopting various spectroscopic and microscopic methods. Further, it pronounces the application of this heterogeneous catalyst for building various bis(hetero/homoarylidene)cycloalkanones from their corresponding carbonyl compounds and cycloalkanones. The model reaction chosen is provided in Figure. 1.3.

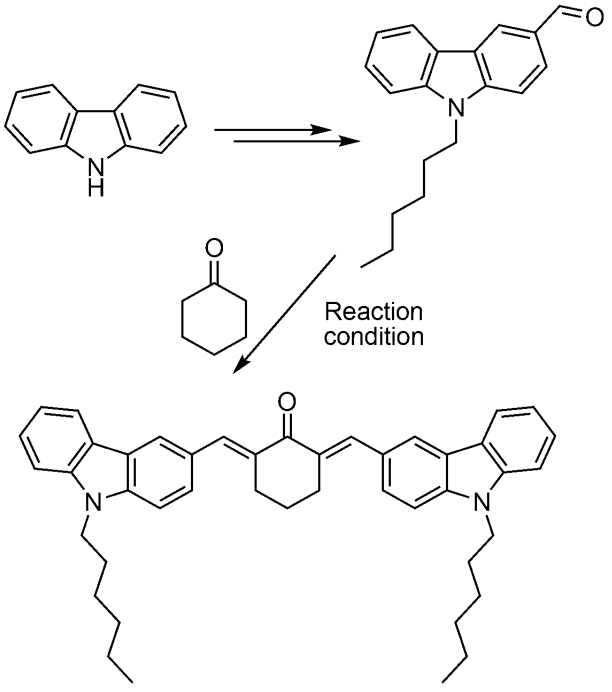

Figure 1.3 Model reaction for the synthesis of bis(hetero/homoarylidene) cycloalkanones

Chapter 6:

This chapter enlightens the results and discussion on characterization of palladium decorated graphitic carbon nitride using various spectroscopic and microscopic methods. Also, it expresses the application of this heterogeneous catalyst for the formation of various bis(hetero/homoarylidene/alkylidene)-1-alkylpiperidin-4-ones from their corresponding carbonyl precursors and 1-alkylpiperidin-4-ones (Figure. 1.4).

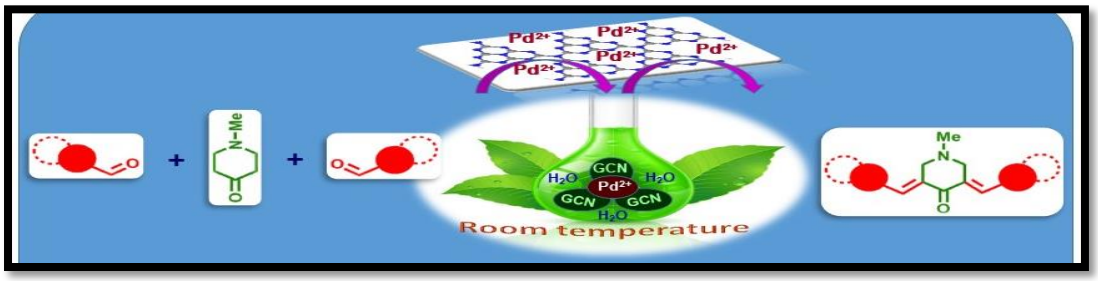

Figure 1.4 Synthesis of bis(hetero/homoarylidene/alkylidene)-1-alkylpiperidin-4-ones

Chapter 7:

It describes the results and discussion on characterization of successfully modified alumina surface with graphitic carbon nitride using various spectroscopic and microscopic methods. Further, it explains the utility of this heterogeneous catalyst for the degradation of methylene blue, a dye which is largely utilized by various industries, under sun light. The pictorial representation for the synthesis of the catalyst is given in Figure. 1.5.

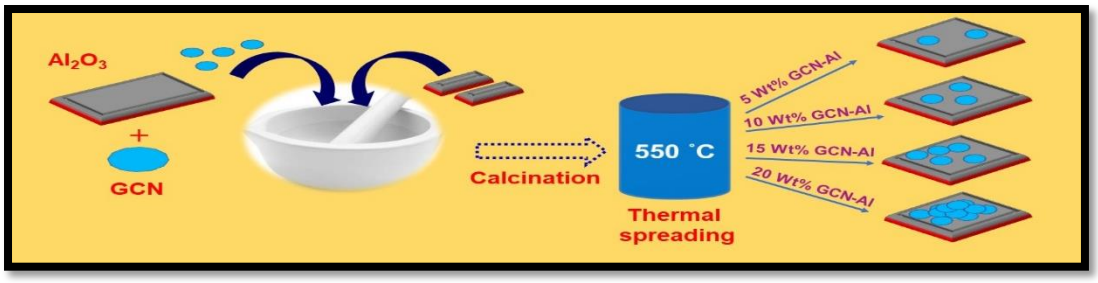

Figure 1.5 Synthesis of alumina surface modified with graphitic carbon nitride

Chapter 8:

This chapter explains the results and discussion on characterization of efficaciously altered ceria surface with graphitic carbon nitride by employing various spectroscopic and microscopic methods. Further, it explicates the use of this heterogeneous catalyst for the degradation of methylene blue, a dye which is largely utilized by various industries, under sun light. The schematic representation for the synthesis of the catalyst is given in Figure. 1.6.

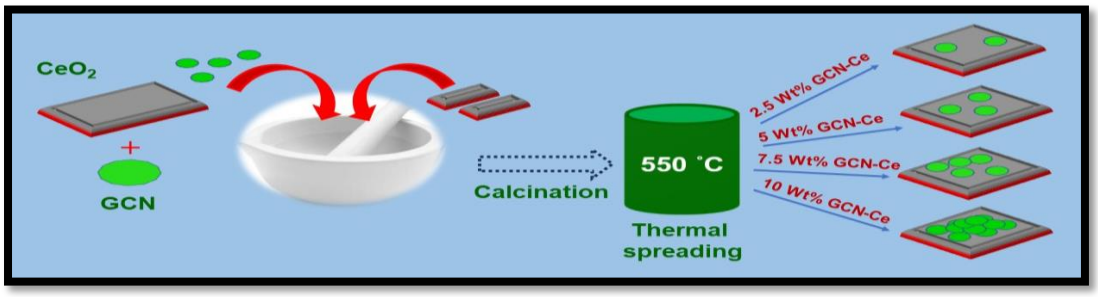

Figure 1.6 Synthesis of ceria surface modified with graphitic carbon nitride

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